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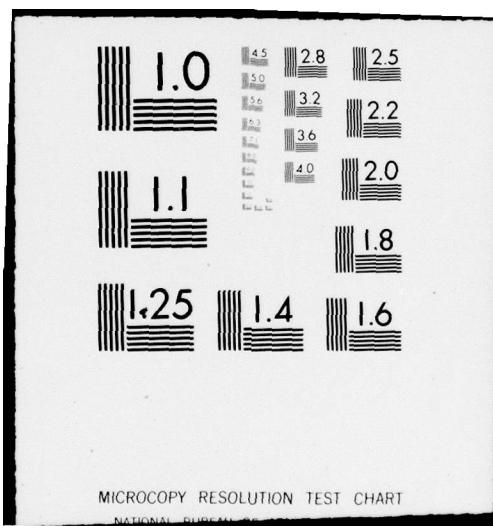
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EFFECTS OF ELECTROCHEMICAL POTENTIAL
ON STRESS CORROSION CRACKING
OF ALUMINUM ALLOY 7079-T6 IN SALT WATER

M. H. Peterson, J. A. Smith, and B. F. Brown

METALLURGY DIVISION

November 1962

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ADDENDUM TO NNL REPORT 1370

Page 3, Line 6 - Strike out "even before" and insert "DUE TO". ✓

Page 3, Line 9 - Insert after first word "(While General cathodic corrosion does not occur before about -1150 MV, pitting due to caustic attack begins at about -950 MV.)" Thus --- ✓

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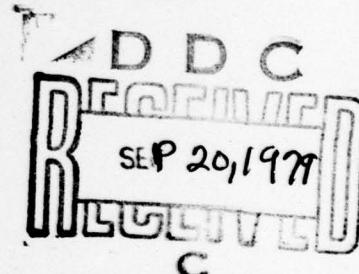
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ABSTRACT

Cathodic protection schemes can greatly extend the useful life of the high strength aluminum alloy 7079, but because of general cathodic wastage at high cathodic currents, cathodic protection cannot produce indefinite immunity to stress corrosion cracking. For long-term applications in sea water requiring this alloy a high-integrity paint system backed up with a galvanic anode system would be indicated for maximum reliability.

PROBLEM STATUS

This concludes one phase of the problem. Work on other phases is continuing.



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INTRODUCTION

The high strength-weight ratio of the 7000-series aluminum alloys has long made them attractive for aircraft construction, and their high compressive-yield strength-density ratio has caused alloy 7079 to figure prominently as a structural alloy for pressure shells for deep marine environments. These pressure shells, proposed or actual, include both manned oceanographic vehicles and unmanned instrument packages. The alloy, however, is alarmingly near conventional aluminum galvanic anodes in general corrosion resistance (or, rather, lack of it), and it is moreover highly susceptible to stress corrosion cracking. Obviously any reliable application of the alloy requires attention to these two corrosion problems. The present study was concerned only with the stress-corrosion problem.

Stress corrosion cracking necessarily involves the flow of small electric currents between "natural" anodic and cathodic areas of an alloy, and as a consequence of this concept sufficient polarization of the cathodic areas by application of external currents might reasonably be expected to render crack formation by stress corrosion impossible (1), and this has been observed in some systems. Recently Brennert (2), for example, studying the stress corrosion cracking of austenitic stainless steels in calcium chloride solutions, observed that a cathodic polarization of only about 50 mv was sufficient to eliminate (for the duration of his experiments) the cracking. Thus cathodic protection techniques offered possibilities for alloy 7079 in applications in which organic coatings were unfeasible or where redundancy was desired.

PROCEDURE

Threaded cylindrical tensile specimens 0.25-in. in diameter were cut from a single plate of 7079 (mill heat-treated in the T6 condition) with the axes of the specimen parallel to the thickness ("short transverse") direction. The ultimate tensile strength was found to be 68,400 p.s.i. and the 0.2% yield strength 52,800 p.s.i. A chemical analysis of the alloy appears in Table 1.

The specimens were degreased in refluxing trichlorethylene and threaded into turnbuckles attached to calibrated steel elastic rings as shown in Fig. 1. This provides a constant tensile load which was set at 40,000 p.s.i. (approximately 75% of the yield strength) for all specimens; in desiccated air a specimen under

this stress did not show cracking or measurable creep in more than 1000 hours of exposure.

A methyl methacrylate cell was positioned around the specimen to confine the corrosion to a 3/4-in. length of the barrel. The electrolyte throughout was 3-1/2% sodium chloride prepared from reagent grade chemical and distilled water; for a few miscellaneous special tests included in Table 2 other chemicals were added to this solution. The electrochemical potential of the specimens was maintained at various levels by directly coupling to galvanic anodes (commercially pure zinc, magnesium, or aluminum-5% zinc) or by employing a potentiostat built by one of us (M. H. P.) which makes use of a galvanic anode. Measurement and/or control of the electrochemical potential at constant levels was obtained by a silver/silver chloride electrode. Since continuous renewal of corrodent was not feasible, daily renewal was adopted to limit the extent of pH drift and accumulation of corrosion products. (See Table 3 for examples of pH drift during experiments in which galvanic anodes were used). It is believed that although corrodent contamination may account in part for some of the scatter in the data, it did not affect the essential conclusions drawn from the study.

RESULTS

Typical failures of aluminum alloy 7079-T6 subjected to a constant tensile load of 40,000 p.s.i. under various exposure conditions are shown in Figure 2. Visual observation did not reveal any appreciable difference in the fracture appearance of specimens whether they were freely corroding or maintained at various potentials as long as they did not undergo gross caustic corrosion, which they did when coupled directly to magnesium.

The results of the experiments on breaking time as a function of potential are shown in Fig. 3 for the straight sodium chloride solution. In addition, some special experiments were conducted in which the solution was altered, or in which the specimen was polarized anodically at high current densities; the results of these are not shown in Fig. 3 but are summarized in Table 2. In Table 2 it can be seen that the hypochlorite which can be generated by the use of inert anodes reduces stress corrosion cracking time, as does also free HCl. Addition of NaOH, on the other hand, lengthens the cracking time. It is to be noted that coupling to mild steel accelerates cracking.

DISCUSSION

(While General Cathodic Corrosion does not occur before about - 1150 MV, pitting due to caustic attack begins at about - 950 MV.)

The results summarized in Fig. 3 clearly show that cathodic protection can greatly retard stress corrosion cracking in 7079, but that it cannot altogether prevent it. The maximum life corresponds to a potential to Ag/AgCl of about - 950 mv, and increasing cathodic polarization beyond this causes a gradual decrease in the life ~~over time~~ the onset of general cathodic corrosion at about - 1150 mv. Thereafter a tensile failure occurs as a reduction in the cross sectional area of the specimen by gross corrosion. Thus it appears that a potential level available from a commercial aluminum-zinc provides maximum stress corrosion resistance and also resistance to general corrosion. It does not appear possible, however, to fully guarantee against stress corrosion cracking of this alloy by electrochemical means, and coatings are thus indicated, though possibly with a galvanic back-up.

It was obvious in advance that an alloy containing aluminum and zinc could not be successfully protected by indiscriminate application of cathodic currents, and the general corrosion observed at high negative potentials was expected. The fundamental reason for the failure to totally prevent stress corrosion cracking of the alloy presumably lies in the heterogeneity of this complex alloy, in combination with the amphoteric nature of the major constituents. The alloy is so complex microstructurally that it appears unwise to try to derive too much fundamental information about stress corrosion cracking from these studies.

SUMMARY AND CONCLUSIONS

Cathodic protection schemes judiciously applied can greatly increase the resistance to stress corrosion cracking of 7079 alloy but cannot altogether prevent cracking. Coatings are thus indicated for long exposure applications, in which cathodic protection would probably be advisable as a back-up scheme. Especially in view of the high sensitivity of the 7079 alloy to stress corrosion cracking perpendicular to the short transverse direction, the findings in the present study are believed to be conservative, and the alloy probably justifies marine experiments in which the short transverse direction is not stressed and in which coatings are backed up with cathodic protection scheme in order to assess the reliability of this combination for lengthy marine service.

REFERENCES

1. J. G. Hines, "On the Propagation of Stress-Corrosion Cracks in Metals", Corrosion Science, Vol. 1, pp. 21-48 (1961)
2. S. Brennert, "Stress Corrosion in Stainless Steels. Effect of Potential Difference Between Liquid and Metal", Jernkontorets Annaler, Vol. 144, p. 560 (1960)

ACKNOWLEDGEMENT

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TABLE 1

Chemical Composition of Alloy

Zn	4.0 %
Mg	3.3
Cu	0.29
Cr	0.23
Mn	0.15
Si	0.08

TABLE 2

Effects of Miscellaneous Conditions on the Stress-Corrosion
Cracking of Aluminum Alloy 7079-T6

General Remarks	Potential Ag/AgCl (mv)	Time to Fracture (Hrs)
Conducted in desiccated air	-	>1000
Freely corroding in 3-1/2% NaCl	840	90.8
Anodically controlled at 20 MA using a Pt cathode	-	1.2
Anodically controlled at 1 MA using a Pt cathode	840	15.3
Minute amount of ClO ⁻ added to 3-1/2% NaCl	840	32.6
Direct couple to mild steel	780	55.7
0.10% HCl added; pH - 2.1	750	8.9
0.10% NaOH added; pH - 11.7	1050	225.0

TABLE 3

A Comparison of pH Drifts During a Twenty-four Hour Period
For Miscellaneous Corrosion Conditions Applied To
Aluminum Alloy 7079-T6

Condition	Initial pH	Final pH
Freely corroding in 3-1/2% NaCl	5.6	6.8
Coupled to aluminum alloy XB605	5.6	8.0
Coupled to commercial zinc	5.6	8.5

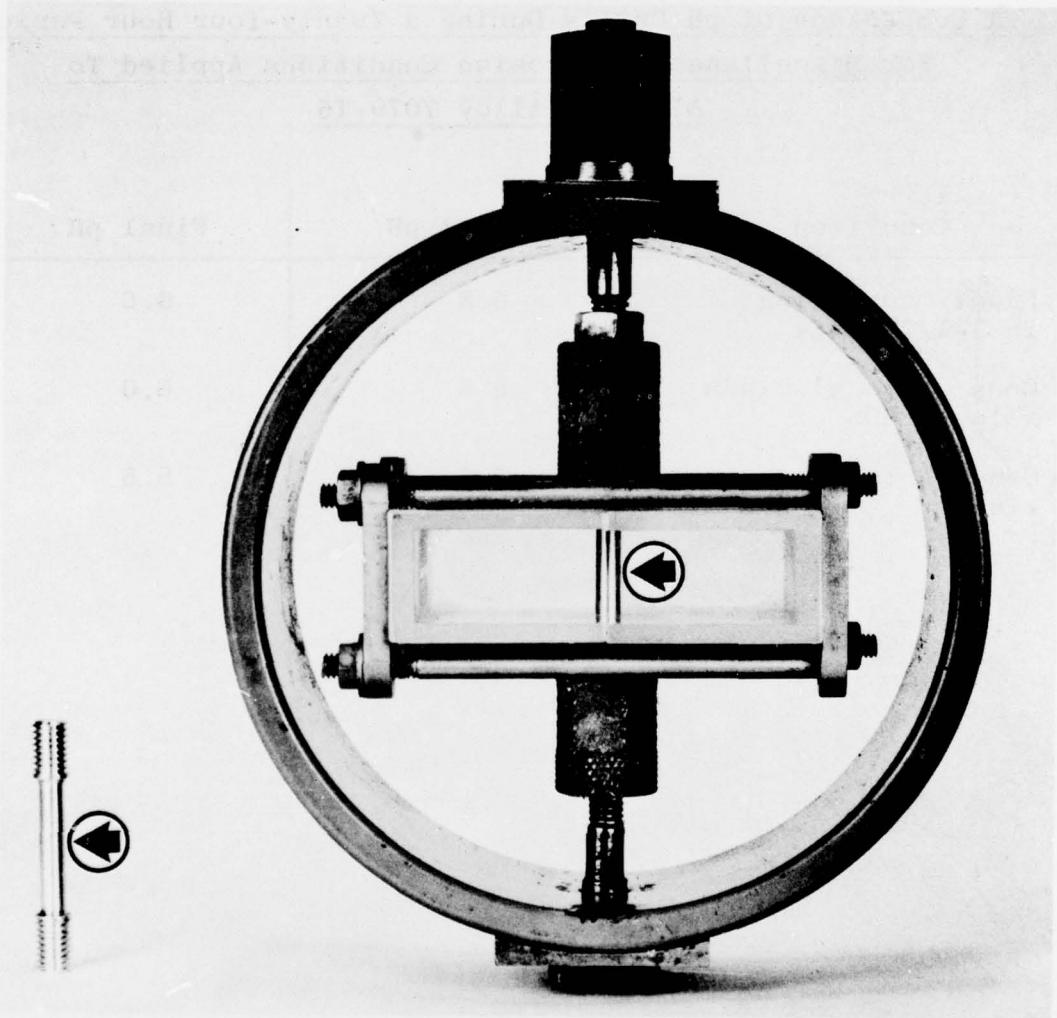


Figure 1 - Specimens (arrows), rectangular plastic cell, and calibrated elastic ring employed to study stress-corrosion cracking

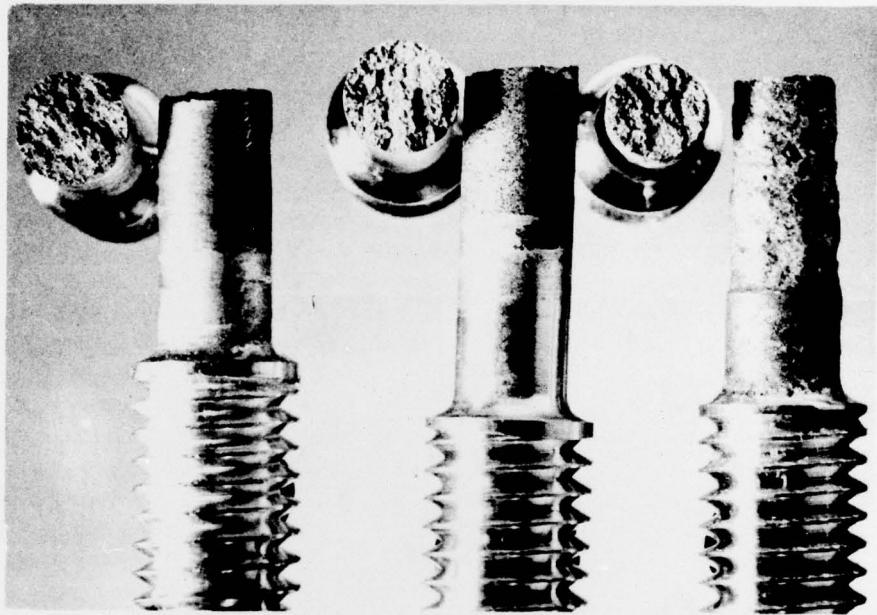


Figure 2 - Fracture of stress-corrosion cracking specimens. Left, freely corroding. Center, potential of -970 mv. Right, coupled to magnesium (-1250 mv).

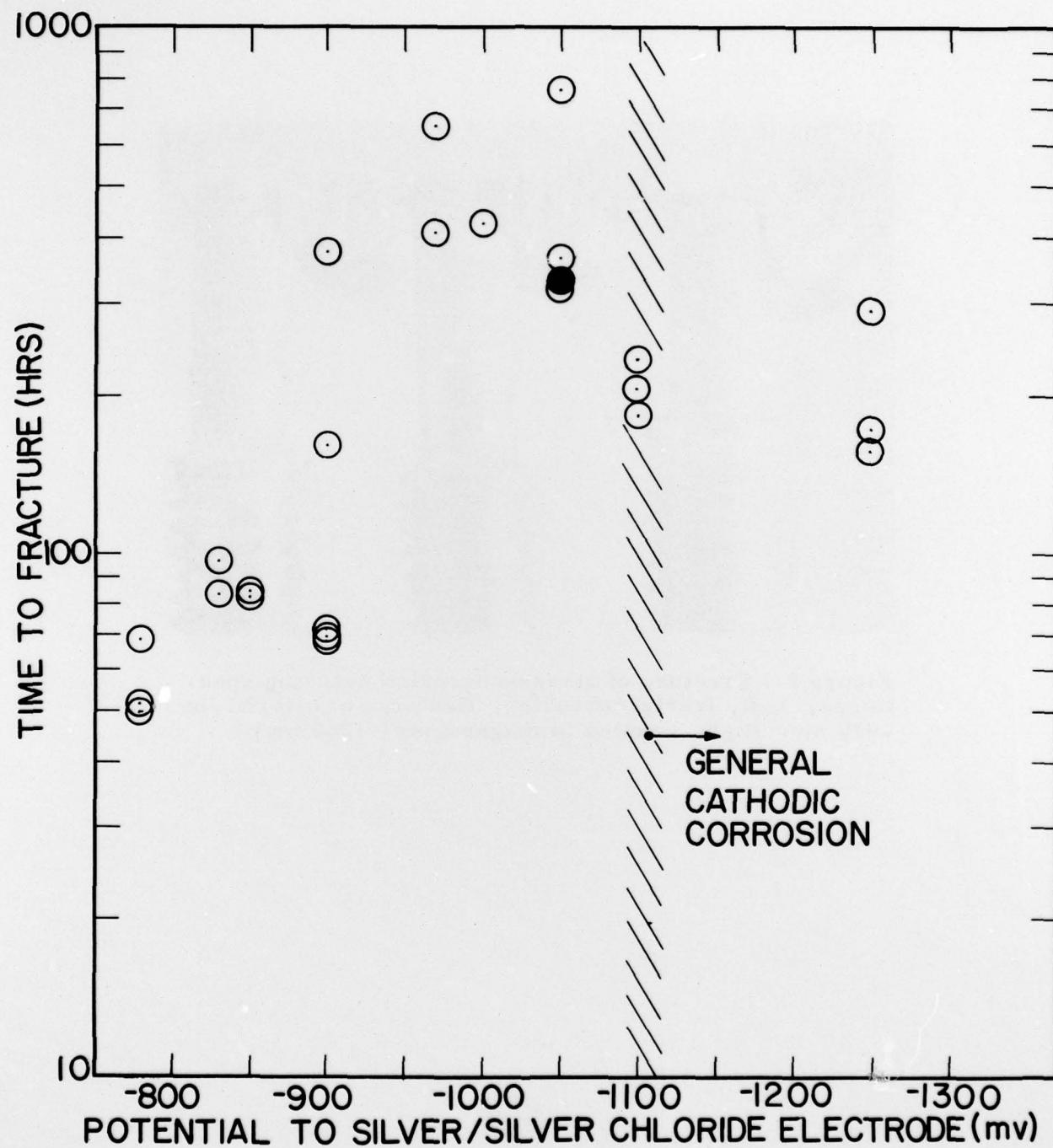


Figure 3 - Effect of electrochemical potential on time to fracture. All specimens in 3-1/2% NaCl. Filled circle indicates experiment with pH adjusted with NaOH to circa 11.7.

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